Study of plasma enhanced chemical vapor deposition of ZnO films by non-thermal plasma jet at atmospheric pressure

AUTHOR(S):

Ito, Yosuke; Sakai, Osamu; Tachibana, Kunihide

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Yosuke Ito*, Osamu Sakai, Kunihide Tachibana

Department of Electronic Science and Engineering, Kyoto University, Kyoto-daigaku Katsura, Nishikyo-ku, Kyoto, 615-8510, Japan

Abstract

Plasma enhanced chemical vapor deposition using a non-thermal plasma jet was applied to deposition of ZnO films. Using vaporized bis(octane-2,4-dionato)zinc flow crossed by the plasma jet, the deposition rate was as high as several tens of nm/s. From the results of infrared spectra, the films deposited at the substrate temperature $T_{\mathrm{sub}} = 100^{\circ}\mathrm{C}$ contained a significant amount of carbon residue, while the films prepared at $T_{\mathrm{sub}} = 250^{\circ}\mathrm{C}$ showed less carbon fraction. The experimental results confirmed that the plasma jet decomposed bis(octane-2,4-dionato)zinc in the gaseous phase and on the substrate, and that there should be the critical T_{sub} to form high-quality ZnO films in the range from 100 to 250°C.

Key words: Zinc oxide, Plasma processing and deposition, Chemical vapor deposition, Fourier transform infrared spectroscopy (FTIR)

*Corresponding author.
Email address: ito_sep25@plasma1.kuee.kyoto-u.ac.jp (Yosuke Ito)

1. Introduction

Plasma processes at atmospheric pressure are promising from the standpoint of developing convenient material processing. However, plasma at atmospheric pressure has a tendency to be localized and to become a thermal plasma with high gas temperature. Such a possibility can be removed by reducing the plasma size and shortening the power-on time of the plasma [1].

From this point of view, an atmospheric pressure plasma jet operated by a low-frequency power source (10 kHz order) in a rare gas has efficient characteristic features, such as a long plasma plume effused into ambient air and low enough temperature to not burn human skin [2]. We have performed various diagnostics of this type of plasma jet, which verified that the gas temperature in the jet is as low as 292 ± 20 K and that the bullet-like plume is driven by the ionization wave through the rare gas channel [3]. Recently, it has been attracting much attention due to its potential for various applications to material processing such as surface modification, dry etching [4] and plasma enhanced chemical vapor deposition (PE-CVD) [5]. In our previous paper [5], we presented an experimental study of PE-CVD of SiO_2 films from tetraethoxysilane (TEOS) using the plasma jet at atmospheric pressure. The deposition rate of SiO_2 films increased with the driving frequency of the plasma jet in a range from 2.5 to 15 kHz, and its best performance reached 280 nm/s at a driving frequency of 15 kHz with the aid of O_3 supply.

In this report, we focus on the deposition of ZnO films using a system to SiO_2 deposition. ZnO has an energy gap of 3.37 eV, i.e. it is transparent to visible light. The oxygen ions (O^{2-}) in the ZnO film easily desorb by changing into oxygen molecules and the electrons are trapped in the film by oxygen

vacancies; namely, ZnO is typically an n-type semiconductor. Additionally, zinc is an abundant natural resource and is not harmful. Therefore, many researchers have tried various methods to deposit high-quality ZnO films as transparent conductive materials [6–9].

In this work, we applied the non-thermal plasma jet to one-dimensional deposition, which is achieved by moving the substrate and useful for roll-to-roll processing, of ZnO films as transparent conductive material, and measured the film quality by Fourier transform infrared spectroscopy (FTIR) and energy dispersive X-ray spectroscopy (EDX).

2. Experimental setup

Figures 1(a) and (b) show the apparatuses used for the deposition of ZnO films using bis(octane-2,4-dionato)zinc ($Zn(OD)_2$, ADEKA Corp.) as the source material, shown in Fig. 1(c). The reasons we have used $Zn(OD)_2$ are that it is liquid at room temperature at the atmospheric pressure for constant supply of source gas, and we cannot use solvents with an ignition point lower than a hundred and several tens of ℃ at atmospheric pressure. We have used two different configurations of our PE-CVD system. Figure 1(a) shows the coaxial configuration of the zinc source supply. The plasma jet shown in Fig. 1(a) consisted of a glass tube of 4-mm inner diameter, equipped coaxially with a stainless steel tube of 3-mm outer diameter. The exit region of the glass tube was pinched to 3-mm inner diameter and a tubular copper electrode of 10-mm length was wound onto it. $Zn(OD)_2$ was heated to 130℃ and vaporized. At this temperature, the partial pressure of $Zn(OD)_2$ was 0.1 Torr. Also, the vaporized $Zn(OD)_2$ was carried to the

process region by helium with a flow rate of 2 L/min and another helium gas flow with 1 L/min. The bipolar impulse voltage [10] with an amplitude of 6 kV_{0p} and driving frequency of 5-30 kHz was applied to the tubular electrode. The substrate was heated to 100 or 250°C by a heater under the substrate stage, which was placed 2 cm below the exit of the plasma jet. By moving this stage at a constant speed of 1 cm/min, we achieved one-dimensional deposition of ZnO.

On the other hand, Fig. 1(b) shows the crossed configuration of the PE-CVD system. The plasma jet consisted of a simple glass tube of 3-mm inner diameter and two tubular electrodes. The distance between the stage and the exit of the plasma jet was about 1 cm. The gas flow rate of helium for the plasma jet was 1.5 L/min and that for carrying $Zn(OD)_2$ was 2 L/min. The distance between the stage and the exit of $Zn(OD)_2$ was 5 mm.

We used three kinds of substrates: silicon; SiO_2/Si, which was made by thermal oxidation; and glass plates to investigate the effects of the property of the substrate surface.

We applied optical emission spectroscopy (OES, USB2000, Ocean Optics Inc.) to the vicinity of the silicon substrate, on which the plasma jet of the coaxial configuration blew. The procedure used in assessing the deposition rate was as previously described [5]. We used a thin-film step-height standard method (XP-2, Ambious Technology) to measure the cross sectional profile of the deposited film, which was a Gaussian-like shape and the maximum height was several hundreds of nm with a full width at half maximum (FWHM) of about 1 mm. The deposition rate was determined from the maximum height by multiplying by the moving speed of the stage and dividing

by the diameter of the plasma jet which was assumed to be equal to the FWHM of the deposited film profile. For film bonding analysis, we applied FTIR (WINSPEC100, JEOL) to the films on silicon substrate. To check the transmittance of the deposited films, we deposited ZnO on glass plates and used a visible-ultraviolet spectrophotometer (V-550, JASCO Corp.)

3. Experimental results

Figure 2 shows the spectra of OES of the coaxial configuration with and without $Zn(OD)_2$. In both cases, there are the spectra related to nitrogen, which constitutes ambient air. In particular, the peaks corresponding to N_2^+ 1st negative system bands ($B^2\Sigma_u^+ - X^2\Sigma_g^+$: 391.4 nm, 427.8 nm, and so on) indicate that the Penning ionization ($He^* + N_2 \rightarrow He + N_2^+(B^2\Sigma_u^+) + e$) occurred. Furthermore, there are also the peaks corresponding to N_2 2nd positive system bands ($C^3\Pi_u - B^3\Pi_g$: 310-360 nm), which might be due to direct excitation of N_2 by electrons. In the case when $Zn(OD)_2$ existed, these peaks decreased little. In contrast, the peaks of helium (707 nm) and N_2^+ 1st negative system bands with the existence of $Zn(OD)_2$ are smaller than those without $Zn(OD)_2$. This fact means that the input power provided to helium in the case of the absence of $Zn(OD)_2$ was put into $Zn(OD)_2$, or that helium excited atoms decompose $Zn(OD)_2$ when $Zn(OD)_2$ exists. Moreover, we could observe many other peaks arising from elements of the ambient air such as O, OH when $Zn(OD)_2$ was absent. These radicals are considered to play an important role in decomposition of $Zn(OD)_2$ in the gas phase and formation of ZnO on the substrate surface. On the other hand, we could not observe the peaks of zinc (467.6, 480.6 nm) [11]. This means that $Zn(OD)_2$

does not sufficiently decompose into zinc atoms and hydrocarbon in the gas phase.

We carried out PE-CVD with the coaxial and crossed configuration. However, the deposited film at the substrate temperature $T_{\mathrm{sub}} = 100^{\circ}\mathrm{C}$ formed no interference pattern and consisted of several hundred nanometer-sized clusters, and that at $T_{\mathrm{sub}} = 250^{\circ}\mathrm{C}$ did not have measurable height (less than 10 nm). It is probably due to too much crystallization of ZnO in the gas phase. Whereas, by using the crossed configuration, we obtained transparent ZnO films. Figure 3 shows the deposition rate of ZnO films with the crossed configuration when one-dimensional deposition was carried out. The thickness of the deposited films was hundreds of nm. The deposition rate of ZnO was lower than that of SiO_2 [5]. It is thought that the molar flow rate of $Zn(OD)_2$ was about 40 times less than that of TEOS, and the fraction of carbon in $Zn(OD)_2$ was higher than that in TEOS. In the case of $T_{\mathrm{sub}} = 100^{\circ}\mathrm{C}$, the deposition rates onto silicon substrates were lower than those onto SiO_2/Si substrates. This is because the plasma, which extended to the dielectric surface, spread widely by accumulated charges on the surface of the substrate with longer residence time.

In the case of $T_{\mathrm{sub}} = 250^{\circ}\mathrm{C}$, the deposition rates onto silicon substrates were lower than those when $T_{\mathrm{sub}} = 100^{\circ}\mathrm{C}$. There are two reasons; one is that the vaporization temperature of $Zn(OD)_2$ is around $200^{\circ}\mathrm{C}$, i.e. $Zn(OD)_2$ is vaporized and blown away from the vicinity of the substrate when $T_{\mathrm{sub}} = 250^{\circ}\mathrm{C}$, and the other is that the high temperature of the substrate causes the migration effect and slows down the deposition rate.

The spectra of FTIR of the deposited films are shown in Figs. 4(a) and

(b). The broad band centered at about 3400 cm^{-1} is attributed to the O-H stretching mode. It also contains the mode due to water trapped in the film. In Fig. 4(a), the peaks centered at 2962 and 2872 cm^{-1} are C-H stretching mode in the methyl group, and those centered at 2926 and 2853 cm^{-1} are that in the methylene group of $Zn(OD)_2$. The peaks of the wave number of 1300-1700 cm^{-1} are the carbonate groups. When $T_{sub} = 250$℃, those peaks originating from C-H and carbonate groups are lower than those in Fig. 4(a). This fact indicates that $Zn(OD)_2$ or its precursors decomposed insufficiently in the gaseous phase deposited on the substrate, and the carbon contained in the precursors forms hydrocarbon and flies out by the effect of heat of the substrate.

Figure 5(a) and (b) show the spectra of EDX of the deposited films. The ratio of zinc to carbon of the deposited film with $T_{sub} = 250$℃ at 30 kHz is higher than that of the deposited film with $T_{sub} = 100$℃ at 5 kHz. Since FTIR spectra have almost no change from changing the driving frequency in the range of 5-30 kHz, the change of the ratio of zinc to carbon is due to the temperature of the substrate.

Figure 6 shows the degree of the transparency of the deposited films, whose thicknesses were several tens of nm, on glass films. The glass substrates are not transmissive for light with a wavelength under 300 nm. Every film has high transparency (more than 90%) in the range from 400 to 900 nm. At less than 400 nm, UV transmittance of the deposited films slightly increased with increase of the substrate temperature. However, the deposited films did not have measurable conductivity by handheld resistance meter, partly because the crystallization of ZnO might be poor in the films and the carrier

mobility might be too small.

4. Discussion

Here we estimate the deposition mechanism roughly from the spatial configuration of the plasma jet crossing with vaporized $Zn(OD)_2$ gas flow. When we assume that $Zn(OD)_2$ is vaporized at the saturation level in the ambient gas, its flow rate to the deposition surface is 1.9×10^{-7} mol/sec. If the supply amount is completely converted into fully crystallized ZnO thin films on the surface with a diameter of 4 mm, which is estimated by the diameter of the plasma jet and $Zn(OD)_2$ supply along with its spreading on the surface, the deposition rate should be 218 nm/s, which is much higher than that observed in the experiment.

In this deposition scheme, convection flux along the gas flow dominates transport of precursors rather than diffusion flux across the gas flow. That is, the key factors for deposition are decomposition rate of $Zn(OD)_2$ at the coalescence region with the plasma jet and sticking rate of the precursors on the surface. To enhance these two rates by plasmas, high electron density as a time-averaged value, efficient electron energy, and activation to yield dangling bonds on the surface might be important issues. When we use this type of plasma jet, the surface activation is much more effective than the conventional plasma jet since the plasma jet becomes a seed to the additional discharge both on grounded metals and dielectrics. That is, if we enhance plasma parameters to decompose more $Zn(OD)_2$ molecules, further high-rate deposition can be expected.

The linear dependence of the deposition rate at the low substrate temper-

ature on the plasma generation frequency indicates that plasmas decompose $Zn(OD)_2$ with a significant amount of residue. A lower deposition rate at the high substrate temperature and change of the EDX spectrum indicate that the organic component was reduced by surface reaction assisted by thermal effects. The rather invariant deposition rate as a function of the plasma generation frequency at the high substrate temperature cannot be discussed using our limited experimental results, but there might be a critical substrate temperature, between 100 and 250°C, at which the deposition mechanism of precursors generated by the plasma changes. Beyond that temperature, it is thought that the carbon contamination in the deposited film is reduced and the UV transmittance of the film improves.

5. Conclusion

We carried out deposition of ZnO films by using a non-thermal plasma jet at atmospheric pressure and obtained a deposition rate of several tens of nm/s, which was more than 10 times higher than that of the conventional deposition schemes. According to investigation of the properties of these films, there was much carbon content originating from source materials. However, the partial carbon component was reduced by heating the substrate to more than 250°C. The transparency of the deposited films was more than 90% in the wavelength range from 400 to 900 nm.

We plan in the near future to improve our method by adding extra oxygen and ozone to remove carbon contamination and by annealing the deposited film to crystallize it.

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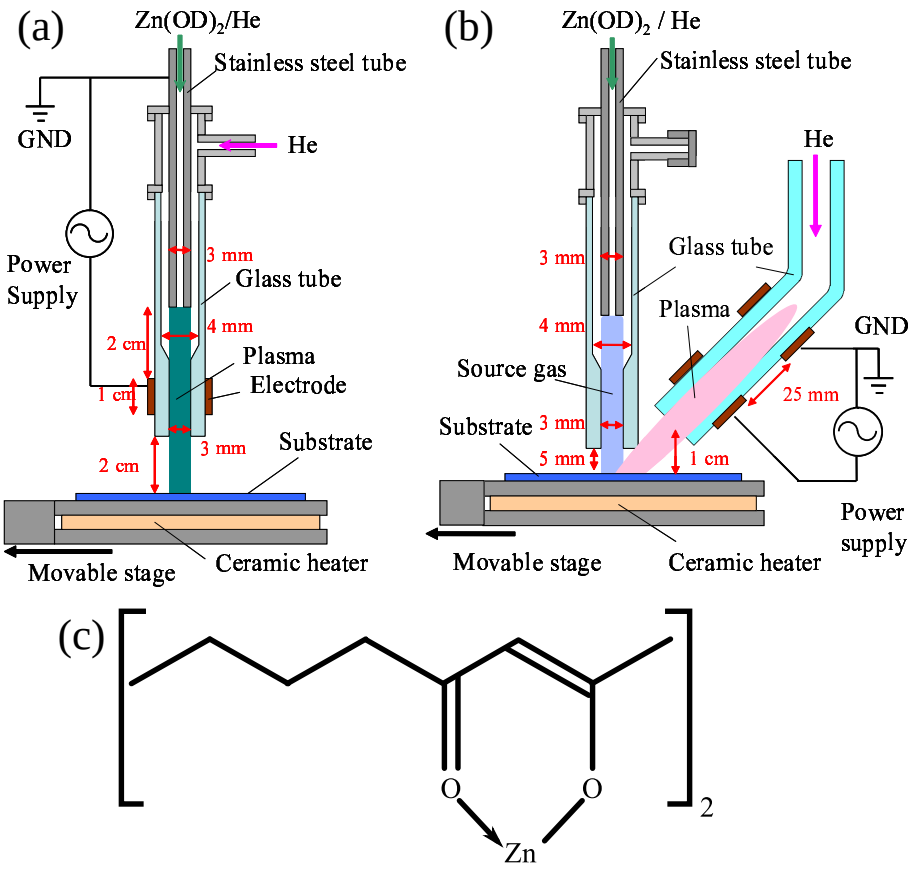
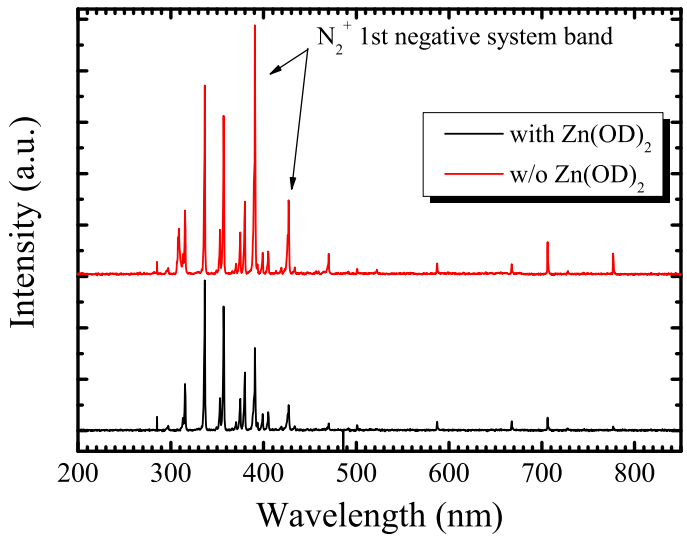


Fig. 1: Schematic drawings of PE-CVD systems. Coaxial configuration (a) and Crossed configuration (b). (c) shows the chemical structural formula of $Zn(OD)_2$.



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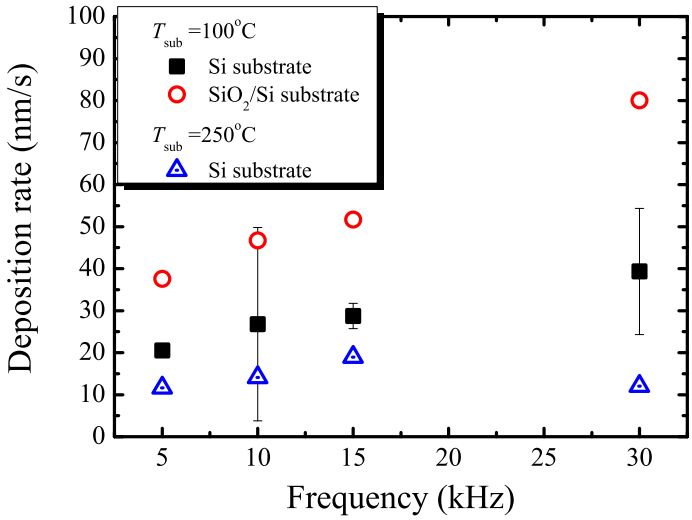
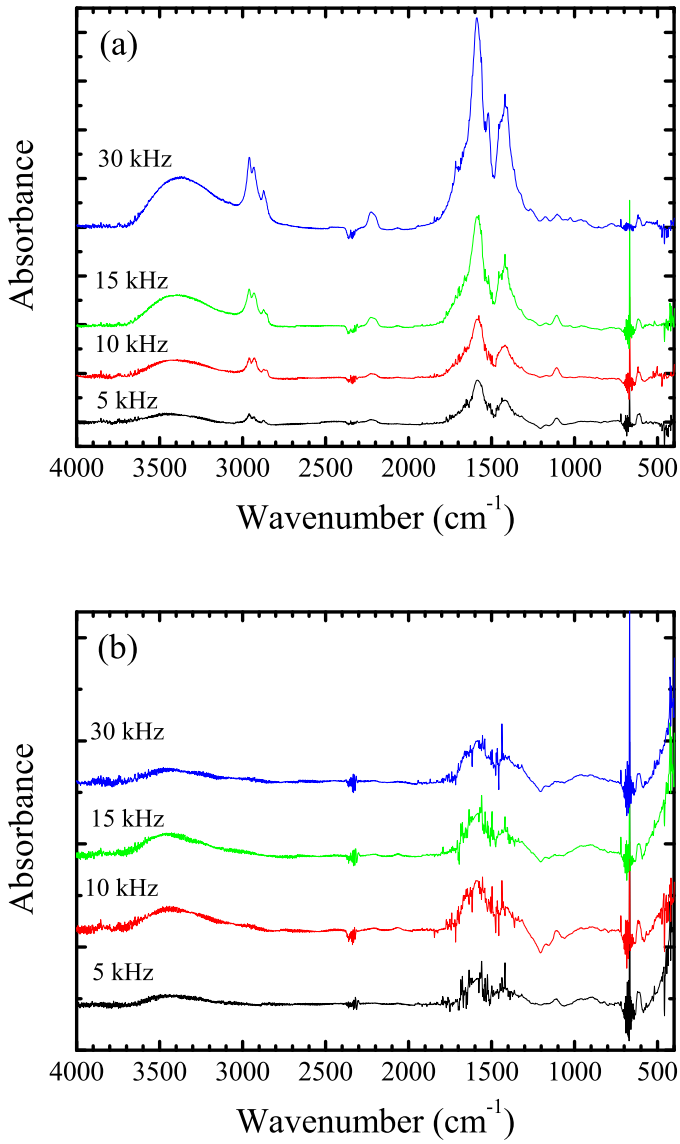


Fig. 3: Deposition rate of ZnO films with the crossed configuration as a function of driving frequency when one-dimensional deposition was carried out.



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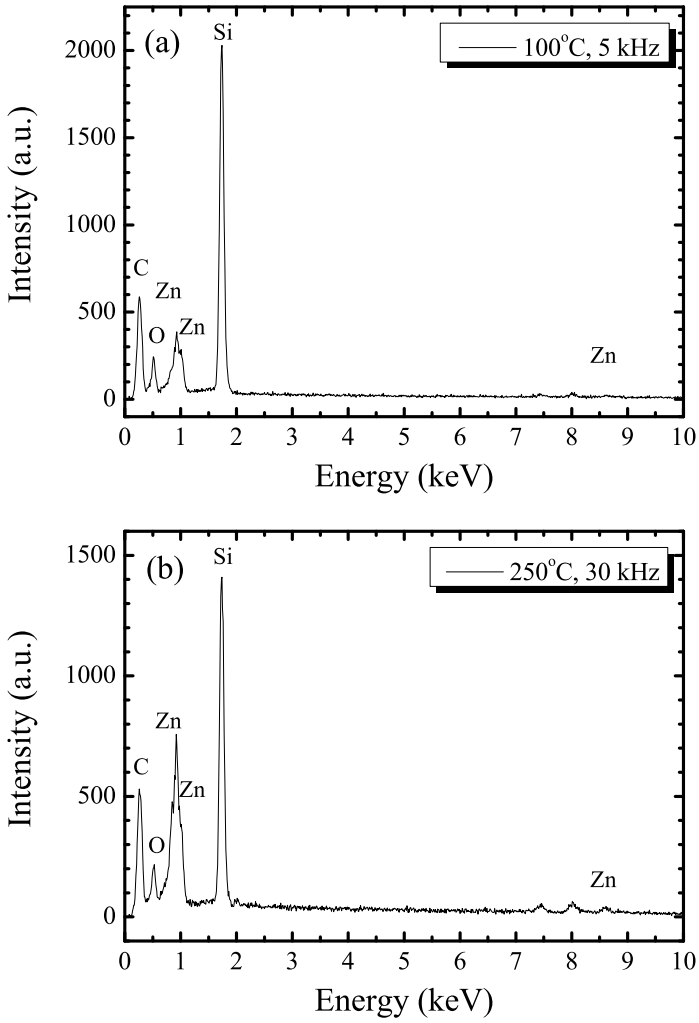
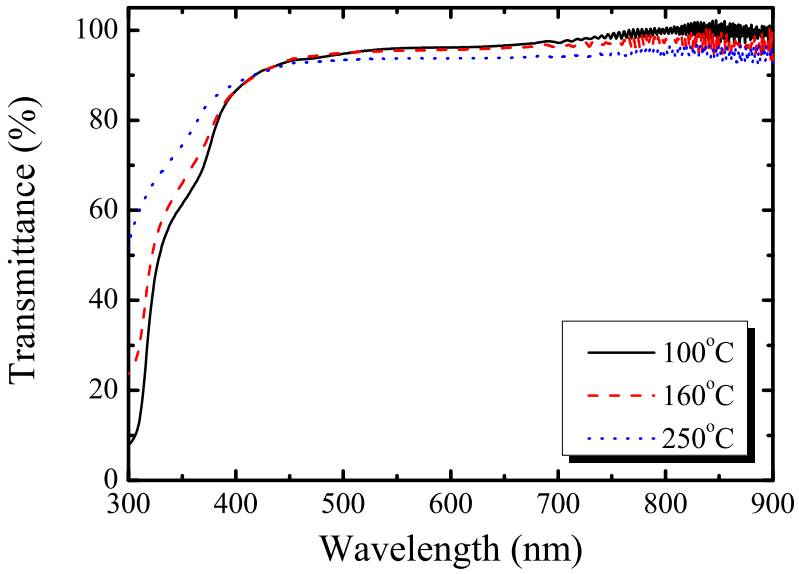


Fig. 5: EDX spectra of deposited films. $T_{\mathrm{sub}} = 100$°C at 5 kHz (a) and $T_{\mathrm{sub}} = 250$°C at 30 kHz (b).



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